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# Polymerization of Acetaldehyde

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(Oda Laboratory)

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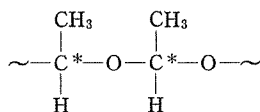
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## 1. INTRODUCTION

In 1936, the polymerization of acetaldehyde was first discovered by Travers and by Letort independently. The discovery of the polymerization was rather accidental. In order to obtain pure acetaldehyde for the studies of thermal- and photo-decompositions, acetaldehyde was vaporized and condensed in a tube immersed in liquid oxygen under high vacuum. During this procedure, it was discovered that acetaldehyde was polymerized when it was frozen. The "freezing polymerization" was unique among polymerization reactions and its kinetics was studied by several groups of workers (Letort, 1951, 1955, 1956, 1960; Rigby et al. 1948; Bevington and Norrish, 1949). After about 20 years studies, it was concluded that the polymerization takes place only when acetaldehyde is in the act of crystallizing at its freezing point.

In 1958, we found that when alumina was used as a catalyst the polymerization occurred without freezing at  $-78^{\circ}\text{C}$ , far above the freezing point of acetaldehyde (Furukawa et al. 1959 a, b, c). The polymer yield by alumina catalyst was much higher than that of the freezing method, and the molecular weight of the polymer produced by alumina catalyst was very high and comparable to that of the freezing method.

Polymers of the freezing method and of alumina catalyzed polymerization are both amorphous and elastic, whose structures have been shown by infrared spectrum to be poly (methyloxymethylene).



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## Polymerization of Acetaldehyde

The investigation of the stereo-chemistry of polyacetaldehyde was stimulated by the progress of the chemistry of propylene polymerization by Ziegler-Natta catalyst. And three research groups, Natta *et al.* (1960 a, b), Vogl (1959, 1960) and we (1959 d, 1960 a, b), independently succeeded in the preparation of crystalline isotactic polymer of acetaldehyde by using metal alkyl catalyst. The attempt to polymerize acetaldehyde by metal alkyl seems to be suggested by the studies of metal alkyl catalyzed polymerization of olefin, diolefin and acrylate monomers. Later, we (1959 d, 1960 a, b) showed that the real active species of the isotactic polymerization is metal alkoxide.

Many papers have been published on the acetaldehyde polymerization. In Table 1 are summarized the catalyst systems or methods of the acetaldehyde polymerization.

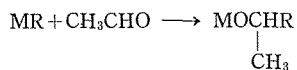
Table 1. Catalysts for the polymerization of acetaldehyde.

Catalyst (or method)	Ref.
<b>Atactic polymer</b>	
Freezing method	{Travers; Letort et al. (1936, '51, '55, '56, '60); Rigby et al.; Bevington et al.
Alumina	{Furukawa et al. (1959 a, b, c); Smidt et al. (1959, '60)
Silica gel	Smidt et al. (1959, '60); Weissermel et al.
Ammonium persulfate	Letort and Mathis (1959)
Polyphosphoric acid-cocatalyst	Miyagawa and Yamamoto
Lewis acid	Vogl (1960)
Metal sulfate-sulfuric acid	Takita and Noro
$\gamma$ -Ray irradiation (in solid)	Chachaty
<b>Isotactic polymer</b>	
Metal alkyl	{Natta et al. (1960 a, b); Vogl (1959, '60)
Metal alkoxide	{Furukawa et al. (1959 d, 1960 a, b)
Alkylaluminum-sodium acetate	Furukawa et al. (1959 d, 1960 a, b)
	Ohta (1963 a)
<b>Stereblock polymer</b> (isotactic and atactic blocks)	
Metal alkyl-alumina	Fujii et al. (1960)
Partially hydrolyzed aluminum alkoxide	Fujii et al. (1960)

In the following part of this article, the latest studies on the polymerization of acetaldehyde in our laboratory are reviewed.

### 2. ALUMINUM COMPOUND CATALYSTS AND THEIR STEREOREGULATING BEHAVIORS

In Table 1, we can see several aluminum compounds; *i.e.*, alumina, aluminum alkyl, aluminum alkoxide, and partially hydrolyzed aluminum alkoxide. It has been discussed that the real active species in the metal alkyl catalyzed polymerization of acetaldehyde is the metal alkoxide which is formed by the reaction between the metal alkyl catalyst and the acetaldehyde monomer (Furukawa et al. 1959 d, 1960 a, b).



In special cases, however, anomalous behaviors of metal alkyl are found. This problem is to be discussed in the following section.

We observed a phenomenon which is common among alumina, aluminum alkoxide and partially hydrolyzed aluminum alkoxide. It is the chemi-sorption of the acetaldehyde monomer on these aluminum catalysts. Fig. 1

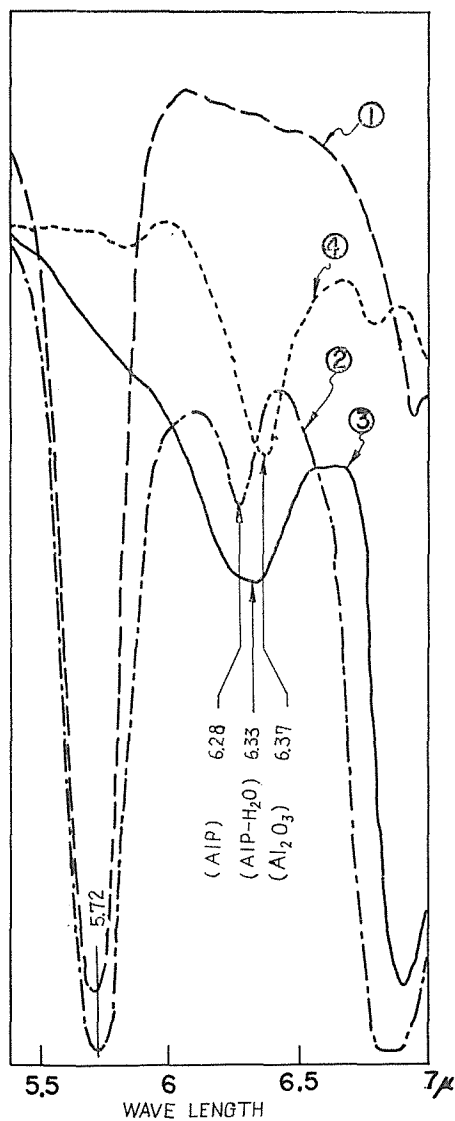


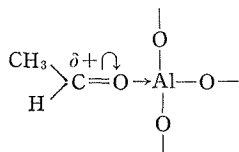
Fig. 1.

- ① ----  $\text{CH}_3\text{CHO}$  (Gas)
- ② -.-.-  $\text{Al}(\text{OPr}^i)_3 \leftarrow \text{CH}_3\text{CHO}$  (n-Heptane solution)
- ③ ———  $[\text{Al}(\text{OPr}^i)_3 \cdot \text{H}_2\text{O}] \leftarrow \text{CH}_3\text{CHO}$  (Nujol)
- ④ .....  $\text{Al}_2\text{O}_3 \leftarrow \text{CH}_3\text{CHO}$  (Nujol)

shows the infra-red spectra of the carbonyl band of acetaldehyde adsorbed by these catalysts. It can be seen that the carbonyl band at  $5.72\mu$  shifts to the region of  $6.2$  to  $6.4\mu$  when acetaldehyde is adsorbed.

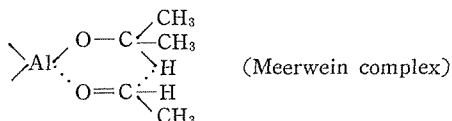
The curve-1 is the spectrum of gaseous acetaldehyde, the curve-2 is that of a mixture of aluminum *isopropoxide* and acetaldehyde in heptane, and the curves-3 and 4 are the spectra of the solid catalysts of partially hydrolyzed aluminum *isopropoxide* and alumina, respectively, which have been treated with acetaldehyde and freed from excess acetaldehyde by vacuum evaporation.

The shift of carbonyl band may be taken to indicate the polarization of carbonyl group by coordination of lone pair electron of oxygen atom.



Furthermore, this polarization seems to be closely related to the activation of the acetaldehyde monomer in the so-called "coordinated anionic mechanism".

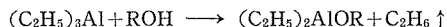
The shift of carbonyl band in the acetaldehyde-aluminum *isopropoxide* system seems to substantiate the *Meerwein-complex* which has been assumed by Meerwein (1936) as a transition state of the Meerwein-Ponndorf-Verley reduction.



There are, however, differences in stereospecificity among these three catalysts. Aluminum alkoxide is the most stereospecific to give isotactic polymer, partially hydrolyzed aluminum alkoxide is the next to produce stereoblock polymer consisting of isotactic and atactic blocks and alumina is the least stereospecific to give atactic polymer. This fact may be explained qualitatively by the assumption that the stereoregulation is accomplished by the steric hindrance of alkoxyl groups in the vicinity of the aluminum active center. The hydrolysis of aluminum alkoxide is carried out in a heterogeneous system, and the alkoxyl groups of the partially hydrolyzed product are not distributed homogeneously along the  $-\text{Al}-\text{O}-\text{Al}-\text{O}-$  linkage. It may be probable that the heterogeneous distribution of alkoxyl group is reflected in the formation of stereoblock polymer.

The assumption that the steric hindrance of alkoxyl group of aluminum alkoxide is essential in stereoregular propagation is supported by our study (Furukawa et al. 1963) in which we carried out a set of polymerization experiments with catalytic systems composed of the reaction products between equimolar amounts of triethylaluminum and various types of alcohols. The product of reaction between equimolar amounts of triethylaluminum and

alcohol has been confirmed to be diethylaluminum monoalkoxide.



The results of polymerization are shown in Table 2. The relative amount of the chloroform-insoluble fraction in the total polymer product is an index of the stereospecificity of the catalyst. In Table 2, it can be seen that the alkoxy group actually controls the stereospecificity of  $(\text{C}_2\text{H}_5)_2\text{AlOR}$  catalysts and that the effect of branching at the  $\alpha$ -carbon atom of alkoxy group predominates over the effects of the length of alkoxy group and of branching at  $\beta$ -position. The X-ray crystallinity of the insoluble fraction varies according to the kind of alkoxy group. Similar variation in stereospecificity of the  $(\text{C}_2\text{H}_5)_2\text{AlOR}$  catalysts according to the alkoxy group was observed in X-ray diffraction.

Table 2. Polymerization of acetaldehyde by  $(\text{C}_2\text{H}_5)_2\text{AlOR}$ .  
(Acetaldehyde, 0.25 mole;  $(\text{C}_2\text{H}_5)_2\text{AlOR}$ , 0.0025 mole; hexane, 20 ml; polymerization was carried out at  $-78^\circ\text{C}$  for 42 hrs.)

RO—	Total yield (%)	Insoluble fraction <sup>a)</sup> (%)
Control	39	16
$\text{CH}_3\text{O—}$	44	32
$\text{CH}_3\text{CH}_2\text{O—}$	36	14
$\text{CH}_3\text{CH}_2\text{CH}_2\text{O—}$	59	22
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O—}$	45	22
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O—}$	44	34
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CHCH}_2\text{O—} \\ \diagdown \\ \text{CH}_3 \end{array}$	35	29
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \\ \diagdown \\ \text{CH}_3 \end{array} \text{CHO—}$	43	49
$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \diagup \\ \text{CH} \\ \diagdown \\ \text{CH}_3 \end{array} \text{CHO—}$	62	79
$\begin{array}{c} \text{CH}_2 \\ \diagup \\ \text{CH} \\ \diagdown \\ \text{CH}_2 \end{array} \begin{array}{c} \text{CH}_2\text{CH}_2 \\ \diagup \\ \text{CH} \\ \diagdown \\ \text{CH}_2\text{CH}_2 \end{array} \text{CHO—}$	29	45
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \\ \diagdown \\ \text{CH}_3 \end{array} \text{CO—}$	12	92

<sup>a)</sup> % of chloroform-insoluble fraction of total polymer.

The stereo-control by alkoxy group seems to be effectuated in the process of co-ordination by the steric hindrance between the acetaldehyde monomer and the alkoxy group around the coordination center. The stereo-control of the alkoxy group over carbonyl compound has also been observed in the Meerwein-Ponndorf-Verley reduction. Doering and Young (1950) reported asymmetric reduction of carbonyl compound by aluminum alkoxide of optically active alkoxide. Jackman *et al.* (1949) made an experiment in which

alkylcyclohexanone was reduced by aluminum isopropoxide to a mixture of epimeric alcohols. Here it was observed that alkylcyclohexanones of higher steric hindrance gave higher selectivity of the *cis*-epimer formation. As has been mentioned, the activated state in which carbonyl group co-ordinate to aluminum may be accepted as being common between the Meerwein-Ponndorf-Verley reduction and the polymerization reaction. Both the asymmetric reduction and stereoregular polymerization are caused by the steric hindrance between the carbonyl compound (acetaldehyde monomer) and alkoxy group.

### 3. CATALYTIC BEHAVIORS OF ALUMINUM ALKYL

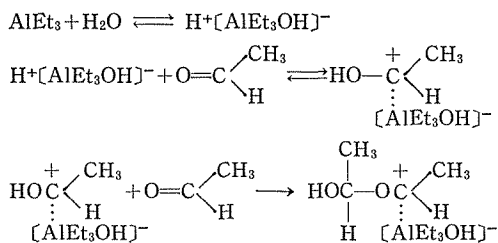
It has been reported that trialkylaluminum induces the isotactic polymerization of acetaldehyde. In this reaction, aluminum alkoxide or dialkyl- or monoalkyl-aluminum alkoxides were assumed to be the real active species inducing the so-called co-ordinated anionic polymerization.

Recently we (Ohta et al. 1963 c) found that triethylaluminum gave only amorphous polymer of acetaldehyde when the polymerization was carried out by introducing the vapor of acetaldehyde gradually to triethylaluminum kept at  $-78^{\circ}\text{C}$  in the absence of any solvent and the mixture was allowed to stand at the same temperature. The product polymer was completely soluble in chloroform, although the degree of polymerization was high enough.

To 2 mmole of  $\text{Al}(\text{C}_2\text{H}_5)_3$  kept at  $-78^{\circ}\text{C}$ , 0.2 mole of pure acetaldehyde was distilled under reduced nitrogen atmosphere, and the mixture was allowed to stand for 20 hrs at  $-78^{\circ}\text{C}$ . Then, the polymerization was stopped by methanol containing pyridine. The yield of polymer was 48.8%, which consisted of 95.7% of methanol soluble and 4.3% of chloroform soluble fraction. Both fractions were shown to be essentially amorphous by infra-red spectrum.

The above result is quite different from that observed before. This contrasts strikingly with the polymerization in which equimolar amounts of triethylaluminum and the acetaldehyde monomer were once reacted with each other at a higher temperature, e.g. room temperature, before the polymerization, and the reaction product was used as catalyst.

It might be seen in Table 1 that cationic catalysts give always amorphous polymer. If we accept this view, it becomes considerably easier to understand the catalytic behavior of trialkylaluminum. That is, trialkylaluminum has a character of Lewis acid, and when its conversion into alkoxide by the reaction with the aldehyde monomer is avoided under a restricted condition it will induce the cationic polymerization through the following scheme.



Natta *et al.* (1960 b, c) reported that a radioactive polymer of acetaldehyde was produced by diethylaluminum ethoxide having labeled ethoxide group but a non-radioactive polymer was obtained by labeled triethylaluminum. This observation may be interpreted by the assumption that the polymerization with diethylaluminum ethoxide catalyst is caused by ethoxide anion probably through the co-ordinated anionic mechanism but that by triethylaluminum catalyst is induced by proton through cationic mechanism illustrated above. If the propagation of cationic polymerization is terminated exclusively by hydroxyl anion, non-radio active polymer should be formed.

We manifested the Lewis acid character of trialkylaluminum in the polymerizations of four- and five-membered cyclic ethers and of vinyl compounds Saegusa *et al.* 1962, 1963 a, b).

Further studies on this problem are being carried out now, and will be published elsewhere.

#### 4. NOVEL CATALYST OF HIGH STEREOSPECIFICITY

Recently we found the reaction product of triethylaluminum and sodium acetate (2:1) to be a highly stereospecific catalyst for the acetaldehyde polymerization (Ohta *et al.* 1963 b).

In 47 ml of benzene, 0.02 mole of  $\text{AlEt}_3$  and 0.015 mole of sodium acetate powder were reacted under nitrogen at  $50\sim 60^\circ\text{C}$  for 2 hours. Sodium acetate, which was insoluble in benzene, went into solution when it reacted with  $\text{AlEt}_3$ . The complex compound obtained as a clear benzene solution was used in the acetaldehyde polymerization at  $-78^\circ\text{C}$  in various organic solvents.

The results of polymerization are shown in Table 3. The reaction between triethylaluminum and sodium acetate was formulated by Ziegler *et al.* (1960) as follows.

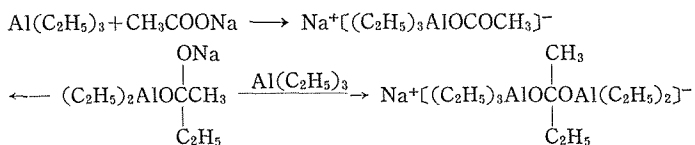


Table 3. Polymerization of acetaldehyde by  $\text{AlEt}_3$ — $\text{CH}_3\text{COONa}$  system.  
(Acetaldehyde, 0.1 mole;  $\text{AlEt}_3$ — $\text{CH}_3\text{COONa}$  complex, 0.0005 mole;  
solvent, 30 ml; Polymerization at  $-78^\circ\text{C}$  for 40 hrs.)

Solvent	Total yield (%)	Fractionation of polymer, (%)		
		$\text{CH}_3\text{OH}$ soluble	$\text{CHCl}_3$ soluble	Insoluble fraction
Hexane	54.1	1.9	1.5	96.6
Heptane	56.5	3.8	2.5	94.7
Toluene	59.5	1.9	1.1	97.0
Benzene	23.2	8.1	5.0	86.9
Ether	72.9	1.0	0.5	98.5
Acetone	11.6	39.9	2.7	57.4



By X-ray and infra-red analyses, the insoluble fractions were shown to be highly stereoregular. The reaction between  $\text{AlEt}_3$  and sodium acetate is known, but the catalytic behavior of this system is not yet understood.

##### 5. TWO-STEP BLOCKCOPOLYMERIZATION OF ACETALDEHYDE WITH PROPYLENE OXIDE (Fujii et al. 1963)

There have been known many catalysts for the acetaldehyde polymerization, and either atactic or isotactic polymer can easily be prepared. At present, a more important problem in polyacetaldehyde is how to stabilize it. Several attempts of stabilization, *i.e.*, end-group acetylation and addition of stabilizer were made. Some of them are effective to a certain extent, but not so enough for the practical application.

One of our techniques is to prepare block-copolymer of acetaldehyde with propylene oxide. By polypropylene oxide block, polyacetaldehyde block was stabilized to a considerable extent.

In order to prepare block copolymer, a technique of two-step polymerization with  $\text{AlEt}_3\text{-H}_2\text{O}$  catalyst was adopted. That is, propylene oxide alone was first subjected to polymerization at room temperature for a fixed time; then the polymerization mixture of the first step was cooled to  $-78^\circ\text{C}$  and acetaldehyde was added to be polymerized at this temperature. The selection of temperatures for this two-step process is based on the fact that below  $0^\circ\text{C}$  the polymerization of propylene oxide hardly proceeds while that of acetaldehyde is possible only below  $-40^\circ\text{C}$ .

Under nitrogen atmosphere, 0.68 ml (0.005 mole) of  $\text{AlEt}_3$  and 0.09 ml (0.005 mole) of water were reacted in 40 ml of hexane at  $0^\circ\text{C}$  for 2 hrs to prepare a catalyst solution, to which 8.6 ml (0.125 mole) of propylene oxide was added. Immediately after 1.5 mins'. polymerization of propylene oxide, the reaction mixture was cooled to  $-78^\circ\text{C}$  and 7 ml (0.125 mole) of acetaldehyde was added. The whole mixture was allowed to stand for 45 hrs at  $-78^\circ\text{C}$ . Then the total polymeric product was extracted successively with methanol and with chloroform.

Table 4 shows the results of two-step blockcopolymerization as well as the reference homopolymerizations of propylene oxide and acetaldehyde. No definite difference in infra-red spectrum was observed between the two-step block-copolymerizate and the acetaldehyde homopolymer. The product of two-step blockcopolymerization, however, left tacky semisolid when it was hydrolyzed with dilute hydrochloric acid at room temperature. The infra-red spectrum of this hydrolysis residue was almost the same as that of polypropylene oxide with the exception of the presence of bands at 1725, 1280 and  $926\text{ cm}^{-1}$  which were to be assigned to carboxyl group<sup>\*)</sup>.

<sup>\*)</sup> Since the intensities of these bands are not changed by washing with water, the carboxyl group possibly is bound to polypropylene oxide molecule. No carboxyl band is observed in the hydrolysis residue of a mechanical mixture of polypropylene oxide and polyacetaldehyde, and therefore carboxyl group seems specific to block copolymer. The mechanism of appearance of this carboxyl group has not been elucidated.

Table 4. Two-step blockcopolymerization of acetaldehyde with propylene oxide by  $\text{AlEt}_3\text{--H}_2\text{O}$  system. $(\text{AlEt}_3\text{--H}_2\text{O} (1:1), 0.005 \text{ mole}; \text{n-hexane}, 40 \text{ ml.})$ .

Monomer (mole)		Polym'n time		Yield of polymer (%) <sup>a)</sup>			
PO	ACH	1st step at r.t. (min)	2nd step at $-78^\circ\text{C}$ (hrs)	$\text{CH}_3\text{OH}$ soluble	$\text{CHCl}_3$ soluble	Insoluble	Total
0.125	0.125	1.5	45	15.2	8.1	1.6	24.9
0.125	0.150	—	45	0.9	0.9	9.4	11.2
0	0.250	—	45	12.8	5.7	9.6	28.1
0.250	0	1.5	45	0.6	0	0	0.6
0.250	0	45 hrs	—	43.3	trace	0	43.3

<sup>a)</sup> Polymer yields are based upon the total amount of the monomers.

The observation that the methanol-insoluble but chloroform-soluble fraction gives methanol soluble polypropylene oxide residue on acid hydrolysis can be taken to indicate the formation of block-copolymer in which polypropylene oxide block is chemically bound to polyacetaldehyde block. In the methanol-soluble fraction of the two-step copolymerization, however, the propylene oxide unit is not always confined only to block copolymer molecules.

The compositions and degrees of polymerization of the methanol-soluble fraction and of the methanol-insoluble but chloroform-soluble one are given in Table 5. Here, the composition was determined by the amount of hydrolysis residue taken as the amount of polypropylene oxide and by elemental analysis, and the degree of polymerization was given by viscosity equations, for polyacetaldehyde (Weissermel and Schmieder 1962)

$$[\eta] = 1.68 \times 10^{-3} M^{0.65} \text{ (in methyl ethyl ketone at } 25^\circ\text{C)}$$

for polypropylene oxide (Ebert and Price 1959)

$$[\eta] = 1.4 \times 10^{-4} M^{0.8} \text{ (in benzene at } 25^\circ\text{C}).$$

Because the content and the degree of polymerization of propylene oxide sequence in the original sample were low, the molecular weight before hydrolysis was calculated by using the viscosity equation of polyacetaldehyde.

From the values of composition and molecular weight, the number of polypropylene oxide block per copolymer molecule was calculated (line a, Table 5). The values in line b are ones corrected by a factor of 0.56 and may give more reliable representations of the original copolymer sample before hydrolysis. The factor corresponds to the observed degree of degradation of a homopolymer of propylene oxide by acid hydrolysis under the same reaction conditions.

These values well indicate that the chloroform-soluble fraction is essentially the blockcopolymer being free from polypropylene oxide. On the other hand, the methanol soluble fraction consists of the homopolymer of propylene oxide and the block-copolymer.

It is to be noted here that the two-step copolymerizate has a higher thermal stability than the acetaldehyde homopolymer and the polymer blend having the same composition.

# Polymerization of Acetaldehyde

Table 5. Composition and degree of polymerization of two-step blockcopolymerization product.

	CH <sub>3</sub> OH soluble fraction	CHCl <sub>3</sub> soluble fraction
Mole % of PO unit		
from hydrolysis	7.9	3.6
from elemental analysis	9.4±2.0	4.9±2.0
Before acid hydrolysis		
[ $\eta$ ]	2.76	3.20
mol. wt.	88,500	111,000
$\bar{P}$	2,000	2,500
After acid hydrolysis		
[ $\eta$ ]	0.105	0.094
mol. wt.	3,930	3,370
$\bar{P}$	70	58
Av. no. of PPO block per polymer chain		
a	1.6	2.5
b	0.9	1.4

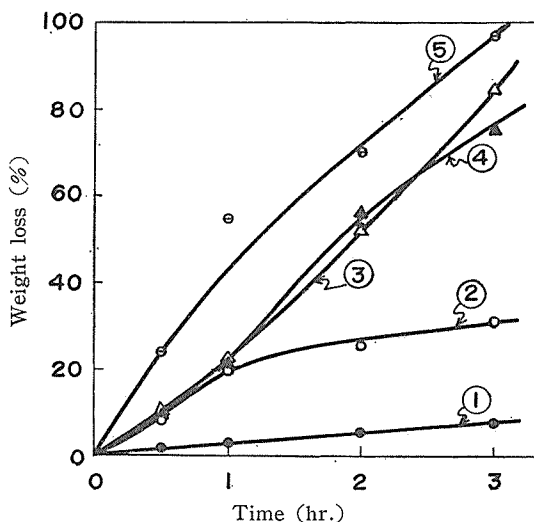


Fig. 2. Thermal degradation of the two-step copolymerizate at 100~102°C. under air.

- Curve 1 (●) : CHCl<sub>3</sub> soluble fraction (Expt. 1-1 ; Table 1)
- Curve 2 (○) : CH<sub>3</sub>OH soluble fraction (Expt. 1-1 ; Table 1)
- Curve 3 (△) : Blend of 95.1 mole-% Polyacetaldehyde ( $[\eta]=3.08$ ) and 4.9 mole-% polypropylene oxide ( $[\eta]=0.15$ )
- Curve 4 (▲) : Blend of 90.6 mole-% polyacetaldehyde ( $[\eta]=3.08$ ) and 9.4 mole-% polypropylene oxide ( $[\eta]=0.15$ )
- Curve 5 (⊖) : Polyacetaldehyde ( $[\eta]=3.08$ )

## 6. SUMMARY

Advance in the study on the polymerization of acetaldehyde was first reviewed, and then our works which were made recently in this field were discussed.

The first topic of our works is on the mechanism of the stereospecific polymerization. We observed the shift of carbonyl band of infra-red spectrum when the acetaldehyde monomer was mixed with aluminum alkoxide catalyst. This observation is taken to show the coordination of acetaldehyde onto the catalyst. Then, the stereospecificities of the catalyst species,  $\text{Et}_2\text{AlOR}$ , were found to depend upon the bulkiness of the OR groups. These findings support the view that stereoregulation in the propagation step is effectuated by the steric hindrance between the adsorbed monomer and the OR groups in close vicinity to the growing center.

The second topic is on the catalytic behavior of aluminum alkyl. It has been known that trialkylaluminum induces the stereospecific polymerization to give isotactic polymer. In this reaction, alkylaluminum alkoxides,  $\text{R}_3\text{-nAl(OR')}_n$  ( $n=1, 2$ ), or aluminum trialkoxide are assumed to be real active species which induce the so-called "coordinate anionic polymerization". We found, however, that trialkylaluminum gave only amorphous polymer when the polymerization was carried out by introducing the acetaldehyde vapor gradually to triethylaluminum kept at  $-78^\circ\text{C}$ . This phenomena was explained by the assumption that trialkylaluminum itself has a Lewis acid character to induce cationic polymerization.

The third topic is on a new catalyst of high stereospecificity, which is the reaction product between triethylaluminum and sodium acetate (molar ratio 2 : 1).

The forth one is the two-step block-copolymerization of acetaldehyde with propylene oxide. With  $\text{AlEt}_3\text{-H}_2\text{O}$  system, propylene oxide was first polymerized at room temperature, and then the reaction mixture was cooled to  $-78^\circ\text{C}$ , by which acetaldehyde was polymerized. Block copolymer thus prepared showed higher thermal stability than that of acetaldehyde homopolymer.

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